*Scientific paper*

# Flocculation and Micellization of Sodium Dodecyl Sulfate Solutions in the Presence of Aluminium Nitrate: Effect of Concentration and Temperature

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***Dedicated to Professor Josef Barthel on the occasion of his 80th birthday***

## Abstract

The present work addresses the question of the effect of the presence of Al(III) on the aggregation and micellization properties of sodium dodecyl sulfate in water. At SDS pre-micellar concentrations, and in the presence of Al(III), aggregation between Al(III) and dodecylsulfate occurs when the ionic concentration reaches equimolar values. Under this condition, the turbidity of the solution increases and is accompanied by a decrease of free SDS in solution and an increase of the bulk pH. This latter result, coupled with data from $^{27}$Al NMR spectroscopy, suggests that the DS$^-$ anion exchanges the hydroxyl ions from the coordination sphere of the hydrolyzed aluminium, and the interfacial pH will decrease upon increasing the DS$^-$ in solution; the formation of aggregates is also supported by the analysis of electrical conductivity data. At concentration ratios greater than around 5, which corresponds to the binding ratio (SDS:Al(III)) value, the dissolution of aggregates occurs upon increasing the SDS concentration.

The effect of Al(III) on the micelle concentration was analyzed using an electrical conductivity technique by calculating the micellization thermodynamic parameters at different Al(III) concentrations and temperatures. It is possible to conclude that in the presence of Al(III) the free energy of micellization ($\Delta G_m^0$) increases; although the critical micelle concentrations of SDS in the presence of aluminium nitrate, for each temperature, are independent of the Al(III) concentration and are lower than the *cmc*, a drastic increase in the degree of micelle counter-ion dissociation is observed. By increasing the temperature, by a system with a constant Al(III) concentration, we have found a decrease in the $\Delta G_m^0$, and as a general trend the dependence of $\Delta G_m^0$ on $T$ decreases upon increasing the salt concentration.

**Keywords:** Aluminum (III), sodium dodecyl sulfate, flocculation, micellization parameters, aggregation.

## 1. Introduction

The study of interactions of ions of high valency with ionic surfactants is of practical importance in areas such as detergency and recovery of surfactants from surfactant-based separation processes.[1–6] Particular relevance stems from the fact that precipitation of ionic surfactants by multivalent counter ions restricts the utilization of ionic surfactants in hard water.

The trivalent ion Al(III) is widely used in various processes involving amphiphilic species. For example, Al(III) has been used as inorganic precursor for the synthesis of mesoporous alumina particles using ionic surfactant aggregates as template[7] and as coagulant agent in the wastewater treatment.[8] Recently, Joubert and In[9] have reported the use of Al(III) for the formation of so-called "tuning interactions" between functionalized micelles.

A number of studies on Al(III)/SDS micelle interactions have been reported. They have shown that Al(III) ions can strongly bind to the micelle surface, leading to a reduction in the surface charge of the micelle[4,5] and an increase in the micelle aggregation number.[10] The micellar surface charge has been reported to reach a minimum at a molar ratio = 0.4, while at concentration ratios greater than 0.4 a change in shape from cylindrical to wormlike aggregates is observed.[1,11,12] However, as far as the authors are aware, no information has been reported concerning the effect of Al(III) on the SDS in the important pre-micellar region.

Our aim is to study how Al(III) can affect the structure of dilute SDS solutions, where SDS is present as unimers (or possible small aggregates). The characterization of these mixed $Al(NO_3)_3$/SDS solutions has been made using techniques such as turbidimetry, $^{27}$Al NMR spectroscopy, potentiometry, and electrical conductivity. The results show that within the SDS pre-micellar region, hydrated Al(III) ions (possible as the hexa-aquo ion) associate with dodecyl sulfate anions. This leads to protonation of hydroxyl anions, present in hydrolyzed forms of Al(III), in the presence of the anionic surfactant.

The free energy of micellization of SDS increases in the presence of Al(III), essentially due to an observed increase in the dissociation degree of micelle counter-ions.

## 2. Experimental Procedure

### 2. 1. Materials

Aluminum nitrate (III) nonahydrate (98.0%, Fluka) and sodium dodecyl sulfate, SDS (Merck, *pro analysis*), were used as received. All solutions were prepared using Millipore-Q water. No control was made on the pH, which was the natural value for each solution (see Results and Discussion section). The NMR samples were prepared by weight using $D_2O$ (99.8%) supplied by Dr Glaser AG (Basel, Switzerland), as solvent.

### 2. 2. Techniques

Turbidity measurements were carried out with a WTW turbidimeter model TURB 355 IR. Turbidity was measured on fresh solutions, and the turbidimeter was calibrated immediately before each experimental run using recommended buffers. The reported experimental values are an average of, at least, two independent measurements.

The $^{27}$Al NMR spectra were obtained on a Varian UNITY-500 NMR spectrometer (at 130.248 MHz) using $Al(NO_3)_3$ acidified at pH 2.0 ($\delta = 0$) as external reference and typically, spectral widths of 8000 Hz, acquisition times of 0.5 s, pulse delays of 0.5 s and about 5000 pulses.

Solution electrical resistance was measured with a Wayne-Kerr model 4265 automatic LC meter at 1 kHz. A Shedlovsky-type conductance cell was used and had a cell constant 0.1181 $cm^{-1}$.[13] Cell constants were measured using the procedure described elsewhere.[14] Measurements were taken at 293.15, 298.15, 303.15, 308.15 and 313.15 (± 0.02) K using a Grant thermostat bath. Solutions were always used within 24 h of preparation. In a typical experiment, 20 mL of $Al(NO_3)_3$ solution were placed in the conductivity cell; then, aliquots of sodium dodecyl sulfate were added using a Metrohm 765 dosimate micropipet. To maintain the concentration of Al(III) constant, the solvent used in the preparation of SDS solution was the same $Al(NO_3)_3$ solution used in the conductivity cell. The conductance of the solution was measured after each addition and corresponds to the average of three ionic conductances, calculated from experimental data using house-made software. Inflexion points observed for the dependence of the electrical conductance of Al(III)/SDS solutions as a function of SDS concentration were calculated using the method of the second derivatives as described elsewhere.[15]

Potentiometric experiments were carried out with a Radiometer PHM 240. The surfactant concentration was measured using a surfactant selective electrode (6.0507.130 Surfactrode Resistant, *Metrohm*) and an Ag/AgCl reference electrode (*Ingold*). pH measurements were carried out with an Ingold U457-K7 pH conjugated electrode; the pH was measured on fresh solutions, and the electrode was calibrated immediately before each experimental set of solutions using IUPAC-recommended pH 4 and 7 buffers.

## 3. Results and Discussion

### 3. 1. Interactions between SDS Unimers and Al(III)

It is well established[1] that the addition of trivalent counterions to SDS micellar solutions leads to further aggregation with a consequent phase separation, while further addition of salt results in the complete dissolution of the complex formed between Al(III) and SDS. Figure 1 shows that a similar process occurs even in the absence of SDS micelles. In fact, an addition of SDS, in the unimer form, to a 1 mM Al(III) solution results in an increase of the sample turbidity with an increase of SDS concentration, reaching a maximum at a [SDS]/[Al(III)] ratio (*r*) of 5.53 (±0.01). At higher concentration ratios a sharp decrease in the solution turbidity is observed. These results suggest that the presence of Al(III) induces the formation of dodecylsulfate ($DS^-$)/Al(III) complex, with a consequent formation of a slightly milky solution. Although this observation occurs at SDS concentration below the *cmc*, this phenomenon is very similar to those formed between micelles and Al(III) and the phase-separation maximum ratio is of a similar order of magnitude to that found when micelles are present ($r = 6.7$).[1] Further, the behavior is similar to what has been reported with aluminium chloride in the presence of alkylsulfonates,[2] where initial precipitate formation is attributed to the aluminium trisulfonate. By comparison with related systems,[16] this corresponds to a sol containing hydrated solid surfactant plus solution. This is then expected to dissolve in the presence of further SDS to form some mixed aggregate or micellar structure. Thus, the precipitation and redissolution of SDS in the presence of Al(III) can be described, respectively, by the following equations:

$$Al^{3+}(aq) + 3\,DS^{-} \rightleftarrows Al(DS)_3(aq)$$
$$Al(DS)_3(aq) + SDS \rightleftarrows \text{mixed micelles}$$

upon constant Al(III) concentration, normal SDS micelles are expected to form upon increasing surfactant.

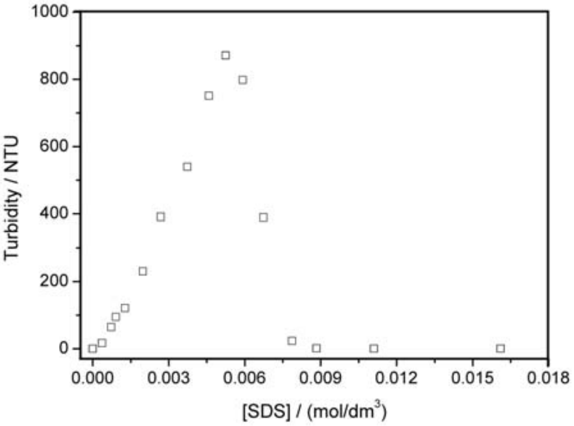

**Figure 1.** Effect of SDS addition on the turbidity of 1.0 × $10^{-3}$ mol/dm$^3$ Al(III) solutions.

To obtain a deeper insight on the mechanism of the interactions that leads to a phase separation and consequent dissolution of these solutions, $^{27}$Al NMR spectroscopy has been carried out on Al(III)/SDS solutions at different concentration ratios, and the corresponding spectra are shown in Figure 2.

These spectra report directly on the coordination behaviour of Al(III), and as can be seen in Figures 2 and 3, differences are observed in the linewidths of the signals. In principle, the linewidths of the $^{27}$Al NMR signals are determined by the quadrupolar relaxation rate of the aluminium nucleus and ligand-exchange processes. The quadrupolar relaxation rate is determined by the interaction between electric quadrupole moment and the electric field gradient at the nucleus. This electric field gradient at the nucleus depends on the number, arrangement and nature of the ligands around the central atom. A symmetrical arrangement of the ligands results in low electric field gradients, hence low relaxation rates and small linewidths. Thus information about the symmetry around a nucleus can be obtained from the observed $^{27}$Al NMR linewidth.

The NMR spectrum of the non-buffered $Al(NO_3)_3$ solution shows a broad peak with a half-height linewidth ($\Delta\nu_{1/2}$) of 109.9 Hz (Fig. 2 A); this broad peak, when compared with that obtained at pH 2 with a $\Delta\nu_{1/2}$ = 9.9 Hz (Fig. 2 F), shows that the Al(III) is present in different complexes in fast exchange equilibrium as a consequence of the metal ion hydrolysis.[17,18] Recent density functional calculations have indicated that hydroxo aluminium(III) complexes may undergo water exchange faster than the corresponding hexaaquo species.[19] However, upon the addition of SDS, at concentrations below the *cmc*, a decrease in the $\Delta\nu_{1/2}$ is observed (Fig. 3). The dependence on the $\Delta\nu_{1/2}$ with *r* seems to follow an exponential decay, with values slowly approaching those at pH 2. This decrease in the value of $\Delta\nu_{1/2}$ is not, however, associated with any significant change in chemical shift, as would be anticipated if it was due to complexing of Al(III) by dodecylsulfate ions. The NMR spectrum at pH 2 can be attributed to $Al(H_2O)_6^{3+}$,[20] where the octahedral structure in a fairly symmetrical chemical environmental is responsible for the narrow linewidth ($\Delta\nu_{1/2}$ = 9.9 Hz, dashed line in Fig. 3). The local pH at interfaces in the presence of anionic surfactants is frequently different from that in bulk solutions,[21] and studies using salicylic acid based indicators and Poisson-Boltzmann simulations[22] indicate that the pH at the surface of SDS micelles is lower than that in bulk solutions. We therefore propose that the observed decrease in NMR linewidth is due to decreasing local pH, and hence a decrease in the degree of hydrolysis of the Al(III) on increasing surfactant concentration. As we shall see later, measurements on the bulk pH are fully consistent with this model. We therefore suggest that $^{27}$Al NMR spectroscopy may, therefore, provide a valuable technique to measure interfacial pH values in aggregating amphiphile systems.

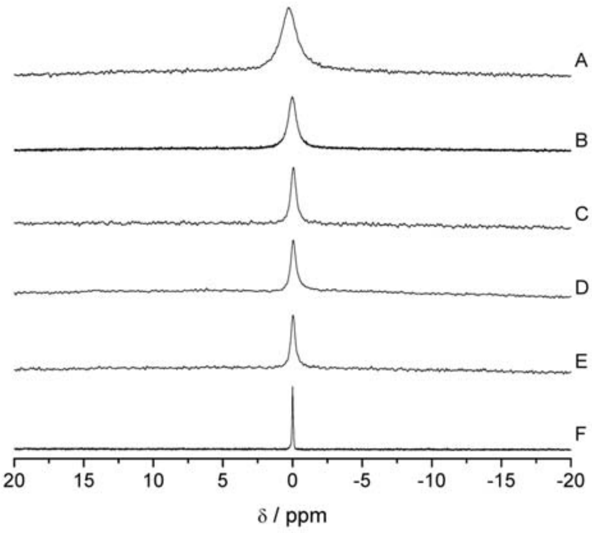

**Figure 2.** $^{27}$Al NMR spectra of different mixed Al(III) 1.079 mmol/kg:SDS $D_2O$ solutions: A) [SDS] = 0 mol/dm$^3$; B) [SDS] = 0.41 × $10^{-3}$ mol/dm$^3$; C) [SDS] = 2.80 × $10^{-3}$ mol/dm$^3$; D) [SDS] = 4.87 × $10^{-3}$ mol/dm$^3$; E) [SDS] = 5.91 × $10^{-3}$ mol/dm$^3$; and F) [SDS] = 0 and pH = 2.

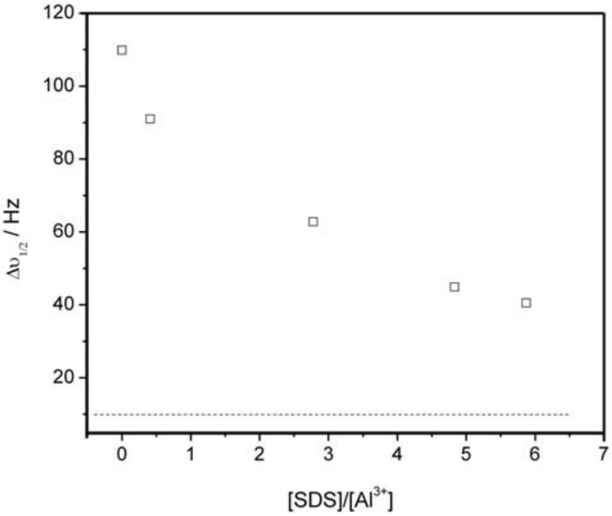

**Figure 3.** Dependence of the half-height linewidth ($\Delta\nu_{1/2}$) on the SDS concentration in the $^{27}$Al NMR spectra of 1.01 × $10^{-3}$ mol/dm$^3$ Al(III)/SDS solutions. Dashed line shows the $\Delta\nu_{1/2}$ of Al(III) at pH 2.

From the electrical specific conductance of aqueous Al(III)/SDS solutions, it is possible to observe different regimes (Fig. 4), corresponding to different zones of Al(III)/SDS interactions. At Al(III) concentrations below 1.01(±0.07) × $10^{-3}$ mol/dm$^3$ (line a – Fig. 4), corresponding to a concentration ratio where equimolar stoichiometry is attained, the electrical conductance of SDS/Al(NO$_3$)$_3$ solutions upon addition of SDS is similar to that of pure SDS in aqueous solutions;[23] however, in the SDS concentration range between 1.01(±0.07) and 4.27(±0.03) × $10^{-3}$ mol/dm$^3$ there is a decrease in the slope of the electrical specific conductance as a function of SDS. This observation can be explained by the formation of larger charged species and/or by the charge collapse of ionic species. Both possible explanations are in agreement with the formation of aggregates involving Al(III) and SDS unimers.

Potentiometric measurements, using a surfactant selective electrode, confirm that the free surfactant concentration drastically decreases from $r = 1.27$ to $r = 2.68$, then remains constant within the range $2.68 < r < 4.2$, and starts to increase again at $r > 4.2$. Although no studies of effect of ionic strength of solutions have yet been done, and with the high charges involved with aggregates these can have a significant effect on the activity coefficients,[24] the potentiometric data are fully consistent with the idea that the interaction between dodecyl sulfate and Al(III) occurs via aggregate/complex formation. It is worthwhile noting that the concentration at which the interaction between unimer dodecyl sulfate anion and Al(III) starts, corresponding to $r = 1.0$, is similar to the concentration region where the onset of flocculation of SDS micelles with Al(III) occurs, according to previous reports.[4,5] In addition, the SDS concentration at which the increase of electrical conductance is observed, $r = 4.3(\pm0.2)$, corresponds to the concentration ratio where the turbidity of the sample decreases sharply. Consequently, at SDS concentrations above 4.27(±0.03) × $10^{-3}$ mol/dm$^3$ (line b – Figure 4) the addition of SDS to Al(III)/SDS solutions behaves in a similar way to other solutions involving trivalent ions;[23,25] that is, an apparent critical micelle concentration ($cmc^{ap}$) is observed, in this case at 11.9 (±0.1) × $10^{-3}$ mol/dm$^3$ – see next section for detailed discussion. The apparent critical micelle concentration corresponds to the experimental concentration at which the onset of SDS micellization, in the presence of salt/aggregates, is observed (line c – Figure 4). This concentration ratio also corresponds to the binding ratio between dodecyl sulfate anions and Al(III) in the aggregates and is similar to those found with other trivalent cations.[25]

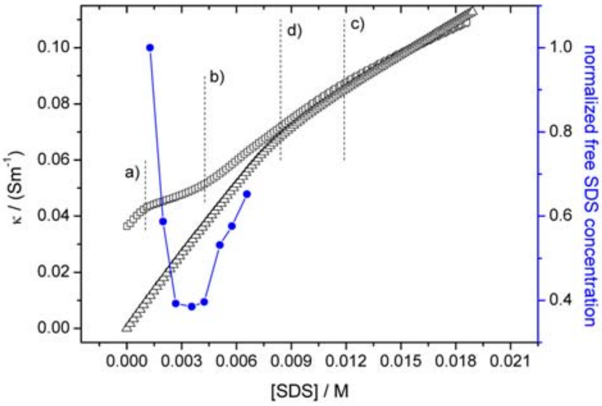

**Figure 4.** Specific electrical conductance, κ, (open symbols) and normalised free concentration (full symbols) as measured by selective electrode potentiometry (o) of SDS in water (Δ) and in aqueous solution of 1 mM Al(NO$_3$)$_3$ at 298.15 K. Vertical dashed lines show inflexion points as seen by electrical conductivity: a) [SDS] = 1.01 × $10^{-3}$ mol/dm$^3$; b) [SDS] = mic = 4.27 × $10^{-3}$ mol/dm$^3$; c) [SDS] = $cmc^{ap}$ = 11.9 × $10^{-3}$ mol/dm$^3$; d) [SDS] = $cmc$ = 8.42 × $10^{-3}$ mol/dm$^3$.

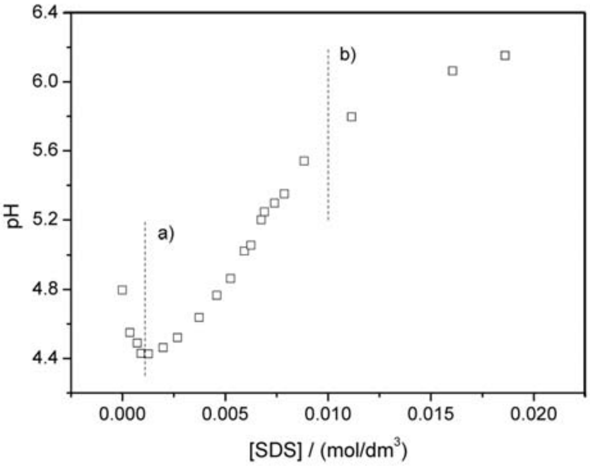

**Figure 5.** pH of 1.0 × $10^{-3}$ mol/dm$^3$ Al(NO$_3$)$_3$/SDS mixed aqueous solutions at 298.15 K. a) [SDS] = 1.1 × $10^{-3}$ mol/dm$^3$, and b) [SDS] = 10 × $10^{-3}$ mol/dm$^3$.

Further information about the interaction mechanism between SDS and Al(III) in these solutions is obtained by potentiometric pH measurements. Fig. 5 shows the pH of Al(III)/SDS aqueous solutions at different concentration ratios. The initial Al(III) nitrate solution has a natural pH of 4.80,[25] which decreases slightly upon initial addition of SDS to 4.43 (a- Fig. 5). This value corresponds to a concentration ratio, $r = 1.1$ (±0.3), which matches with the beginning of interaction between SDS and Al(III) observed by electrical conductivity. Further additions of SDS lead to an increase in bulk pH that corresponds to a decrease in interfacial pH that parallels the decrease in linewidth in the $^{27}$Al NMR spectra shown in Figure 3. This is in complete agreement with a partitioning of $H^+$ ions towards the anionic dodecylsulfate upon aggregate formation.

It is interesting to note that at [SDS] = 10 (±1) × $10^{-3}$ mol/dm$^3$ there is a second inflexion point in the plot of p-H as a function of $r$ (b in Figure 5), which corresponds to the SDS $cmc^{ap}$. This value is in reasonable agreement with the value obtained by electrical conductivity (11.9 (±0.1) × $10^{-3}$ mol/dm$^3$).

## 3. 2. Effect of Initial Concentration of Al(III) and Temperature on the Micellization Properties of SDS

In the previous section we have shown that aggregation of Al(III) with dodecyl sulfate can occur in a region below the pure surfactant *cmc*, and that this affects the degree of hydrolysis of the Al(III) ion.

A further relevant point is whether the presence of these aggregates may affect the micellization properties of SDS. To evaluate such phenomena, a set of physical chemical parameters have been calculated to obtain an insight about the mechanism of SDS micellization in the presence of different initial Al(III) concentrations, at different temperatures (ranging from 293.15 to 313.15 K). The experimental results for us to perform such analysis were obtained by electrical conductivity measurements. This technique has been shown to be a simple and reliable technique to follow the alteration in the structure of metallic ion/surfactant solutions[23,26] – see Figure 4.

Table 1 shows the micellization parameters, the critical micelle concentration (*cmc)* and degree of micellar counterion dissociation ($\alpha$) of SDS under different experimental conditions. The critical micelle concentration of SDS, in the presence of Al(III), *cmc'*, was calculated as a difference between the $cmc^{ap}$ (c in Fig. 4) and the maximum interaction concentration of SDS with Al(III), *mic* (b in Fig. 4), assuming that the *mic* is the surfactant concentration necessary for complete association with all the Al(III) present in solution. A second micellar characteristic which is likely to depend on the presence of other ionic species is the $\alpha$. $\alpha$ values were calculated from the ratio between the slopes of the postmicellar and premicellar regions, i.e. after and before line c in Fig.4, respectively, in the plots of $\kappa = f([SDS])$.[27] From data shown in Table 1, we can see that in the absence of Al(III) the experimental values reported here are in good agreement with those reported in literature.[28–30] In solutions containing Al(III), or Al(III)/DS$^-$ aggregates, we can conclude that: a) the *cmc'* of SDS is lower than the *cmc*, as expected from the presence of an electrolyte;[31] b) the *cmc'* is almost independent of temperature and initial Al(III) concentration; and c) the degree of dissociation of micelle counter-ions in-

**Table 1:** Micellization experimental values of SDS at different temperatures in the presence and absence of Al(III).

| | | | ***T*** | | |
|---|---|---|---|---|---|
| | **293.15** | **298.15** | **303.15** | **308.15** | **313.15** |
| [Al(III)] = 0 | | | | | |
| *cmc*/mM | 8.51 (0.03) | 8.42 (0.03) | 8.48 (0.03) | 8.58 (0.03) | 8.69 (0.03) |
| $cmc^a$/mM | 8.449 | 8.378 | 8.427 | 8.546 | 8.875 |
| $a$ | 0.440 (0.001) | 0.459 (0.001) | 0.455 (0.002) | 0.469 (0.001) | 0.471 (0.001) |
| $a^b$ | | 0.41 | 0.430 | | 0.457 |
| [Al(III)] = 0.5 mM | | | | | |
| $cmc^{ap}$ /mM | 10.6 (0.1) | 10.4 (0.1) | 10.5 (0.1) | 10.5 (0.1) | 10.6 (0.1) |
| *cmc'* /mM | 7.4 (0.2) | 7.2 (0.1) | 7.4 (0.2) | 7.4 (0.1) | 7.3 (0.2) |
| $a$ | 0.545 (0.002) | 0.546 (0.002) | 0.550 (0.003) | 0.555 (0.002) | 0.559 (0.002) |
| [Al(III)] = 0.75 mM | | | | | |
| $cmc^{ap}$ /mM | 11.2 (0.1) | 11.3 (0.1) | 11.5 (0.1) | 11.5 (0.1) | 11.6 (0.1) |
| *cmc'* /mM | 7.59 (0.09) | 7.64 (0.09) | 7.8 (0.1) | 7.8 (0.1) | 7.8 (0.2) |
| $a$ | 0.570 (0.002) | 0.585(0.002) | 0.593 (0.003) | 0.602 (0.002) | 0.605 (0.003) |
| [Al(III)] =1 mM | | | | | |
| $cmc^{ap}$ /mM | 12.0 (0.1) | 11.9 (0.1) | 12.0 (0.1) | 12.1 (0.1) | 12.2 (0.1) |
| *cmc'* /mM | 7.8 (0.2) | 7.6 (0.1) | 7.7 (0.2) | 7.8 (0.2) | 8.0 (0.1) |
| $a$ | 0.601 (0.004) | 0.604 (0.004) | 0.620 (0.003) | 0.639 (0.005) | 0.642 (0.003) |

The values inside parentheses are standard deviations. $^a$ values taken from ref. 26; $^b$ values taken from ref. 29.

creases with temperature and with Al(III) concentration.

These last two observations can be readily justified by the screening effect provoked by the presence of trivalent ions and/or by the release of nitrate ions by aluminium nitrate upon association with dodecyl sulfate anions. Since *T* and ionic strength have opposite contributions to the *cmc'*,[31] it is not surprising that the balance between them will lead to the observed constant *cmc'*; however, these two properties lead to an increase in α. The increase in α with *T* seems reasonable, and does not require further explanation. However, the effect of ionic strength is less clear. Probably the observed increase in the degree of dissociation may result either from an increased screening effect produced by the existence of free ions in solutions in a high ionic strength media,[32] or by micelle growth in the presence of salt.[33,34]

To obtain further insight into the SDS micellization mechanism and on the balance of forces involved in micelle formation, a thermodynamic analysis has been carried out.

The standard Gibbs free energy and enthalpy of micellization ($\Delta G_m^0$ and $\Delta H_m^0$) of SDS in the absence and in the presence of the electrolyte were calculated by using[28,35]

$$\Delta G_m^0 = (2-\alpha)RT\ln X \qquad (1)$$

and

$$\Delta H_m^0 = -RT^2[(2-\alpha)\frac{d\ln X}{dT} + \ln X\frac{d(1-\alpha)}{dT}] \qquad (2)$$

where *X* is the *cmc* (or *cmc'* for solutions containing Al(III)) in mole fraction units, and the other symbols are as previously indicated.

From data shown in Table 1, we can conclude that ln *X* is independent of temperature, with values –8.78 (±0.01), –8.93 (±0.01), –8.88 (±0.02) and –8.78 (±0.01), for 0 to 1.0 × $10^{-3}$ mol/dm$^3$ Al(NO$_3$)$_3$-containing solutions, respectively. Consequently, Eq. (2) can be simplified to

$$\Delta H_m^0 = -RT^2(\ln X\frac{d(1-\alpha)}{dT}) \qquad (3)$$

The dependence of the degree of counter-ion binding (1-α) on *T* was determined using a linear least-squares procedure; the following slopes were obtained: –1.7(0.2) × $10^{-3}$ K$^{-1}$, –7.6(0.8) × $10^{-4}$ K$^{-1}$, –1.8(0.2) × $10^{-3}$ K$^{-1}$ and –2.1(0.2) × $10^{-3}$ K$^{-1}$, for solutions containing 0, 0.5, 0.75 and 1.0 × $10^{-3}$ mol/dm$^3$ Al(NO$_3$)$_3$, respectively.

The entropy of micellization was evaluated from

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \qquad (4)$$

Table 2 summarizes the corresponding micellization thermodynamic data for SDS/Al(NO$_3$)$_3$ systems.

From data shown in Table 2, the following observations can be made: a) SDS micellization is favoured by increasing the temperature; b) the dependence of $\Delta G_m^0$ with temperature decreases upon increasing the salt concentration; c) for each salt concentration, $\Delta H_m^0$ and $\Delta S_m^0$ decrease with temperature;[36] and d) in the absence of aluminium nitrate, the SDS micellization is entropy-driven, i.e. the contribution of $|\Delta H_m^0|$ to the Gibbs free energy is less than that of $|T\Delta S_m^0|$; however, upon increasing the salt concentration, both the enthalpy and entropy contributions to the Gibbs free energy of micellization are balanced. This last result strongly suggests that in the presence of the highest

**Table 2:** Effect of aluminium nitrate on the thermodynamic parameters of SDS at various temperatures.

| | ***T*** | | | | |
|---|---|---|---|---|---|
| | **293.15** | **298.15** | **303.15** | **308.15** | **313.15** |
| [Al(III)] = 0 | | | | | |
| $\Delta G_m^0$ / (kJ mol$^{-1}$) | –33 | –34 | –34 | –34 | –35 |
| $\Delta H_m^0$ / (kJ mol$^{-1}$) | –11 | –11 | –11 | –12 | –12 |
| $\Delta S_m^0$ / (J K$^{-1}$ mol$^{-1}$) | 78 | 76 | 75 | 74 | 72 |
| [Al(III)] = 0.5 mM | | | | | |
| $\Delta G_m^0$ / (kJ mol$^{-1}$) | –32 | –32 | –33 | –33 | –34 |
| $\Delta H_m^0$ / (kJ mol$^{-1}$) | –5.0 | –5.0 | –5.2 | –5.4 | –5.5 |
| $\Delta S_m^0$ / (J K$^{-1}$ mol$^{-1}$) | 91 | 91 | 90 | 90 | 89 |
| [Al(III)] = 0.75 mM | | | | | |
| $\Delta G_m^0$ / (kJ mol$^{-1}$) | –31 | –31 | –31 | –32 | –32 |
| $\Delta H_m^0$ / (kJ mol$^{-1}$) | –11 | –12 | –12 | –13 | –13 |
| $\Delta S_m^0$ / (J K$^{-1}$ mol$^{-1}$) | 67 | 65 | 63 | 62 | 61 |
| [Al(III)] = 1 mM | | | | | |
| $\Delta G_m^0$ / (kJ mol$^{-1}$) | –30 | –31 | –31 | –31 | –31 |
| $\Delta H_m^0$ / (kJ mol$^{-1}$) | –13 | –14 | –14 | –15 | –15 |
| $\Delta S_m^0$ / (J K$^{-1}$ mol$^{-1}$) | 58 | 57 | 55 | 53 | 51 |

Al(III) salt concentration the hydrophobic effect is not the dominant factor in the micellization process.

## 4. Conclusions

The presence of SDS in the unimer form induces the formation of Al(III)/dodecyl sulfate aggregates. These aggregates are formed at concentration ratios ([SDS] /[Al(III)]) greater than 1.The mechanism of aggregate formation is to be found in the decrease of the Al(III) degree of hydrolysis as a function of SDS concentration, as seen by $^{27}$Al NMR. At concentration ratios greater than around 5 the behavior of SDS is fairly similar to that occurring in Al(III) salt free solution; consequently this value corresponds to the binding ratio between Al(III) and dodecyl sulfate anions. From the analysis of the micellization thermodynamic parameters of SDS in the presence of Al(III) and at different temperatures we may conclude: a) the entropy factor dominates the temperature effect on the free energy of micellization and b) by increasing the aluminium salt concentration the free energy of micellization becomes less dependent on the temperature.

## 5. Acknowledgments

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## Povzetek

Raziskovali smo vpliv Al(III) na procese agregacije in micelizacije natrijevega dodecil sulfata (SDS) v vodi. Ugotovili smo, da v območju nizkih koncentracij v prisotnosti ekvimolarnih koncentracij Al(III) in SDS poteče agregacija med Al(III) in SDS. Opazna je naraščajoča motnost raztopine, ki jo spremlja zmanjšanje prostih SDS molekul v raztopini in hkrati zvišanje pH vrednosti raztopine. S pomočjo podatkov v literaturi, dobljenih z NMR spektroskopijo, lahko sklepamo na izmenjavo DS$^-$ ionov s hidroksilnimi ioni iz hidratnega sloja Al(III). Ob povečanju koncentracije SDS agregati očitno razpadejo.

Vpliv Al(III) na micelizacijo SDS smo raziskovali z meritvami električne prevodnosti pri različnih temperaturah, ki nam omogoča tudi izračun termodinamskih parametrov micelizacije. Izkazalo se je, da prisotnost Al(III) v raztopini zviša Gibsovo prosto energijo micelizacije ($\Delta G_m^0$). Opaziti pa je izredno povečanje stopnje disociacije micele-protiion, čeprav je kritična koncentracija agregacije praktično neodvisna od koncentracije Al(III) in precej nižja od kritične micelne koncentracije.